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XXV. *Researches on Silica.* By Colonel PHILIP YORKE, F.R.S.

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SINCE chemistry has been studied as a science, it has been an object with its cultivators to arrange the bodies which have been the subjects of their attention, into groups in which the individuals should have a natural relation to each other. Probably at no time in the history of the science has the importance of such a classification been more strongly felt than at the present day, not only on account of the number of known elements, but also from the number of compound bodies appearing to act as elements, which organic chemistry has made known. Although great advances have been made in this direction, the place of the element silicon in such a series as above alluded to, is very doubtful. Yet the binary compound of this element, silicon with oxygen, is familiar to every one; it constitutes by itself a considerable portion of the crust of the earth, and enters into a long series of definite crystallized compounds.

It has been satisfactorily determined that this substance, silica, belongs to the class of bodies designated as acids, but one essential point is wanting to enable chemists to give it, or its peculiar element, its proper position, and that is, the formula of this silica or silicic acid.

Three different formulas have been proposed and made use of by different chemists,—
 SiO_3 , SiO_2 , SiO .

The first was originally adopted by BERZELIUS, from a consideration of the composition of felspar; and subsequently it was supported by arguments deduced from a law relating to the boiling-points of the volatile compounds of chlorine and bromine, suggested by HERMANN KOPP. The composition of a compound of chlorine, sulphur and silicon, discovered by IS. PIERRE*, is also favourable to this formula. The second formula is adopted by GMELIN, and is supported by some experiments of H. ROSE†, who found that when silica is fused with excess of carbonate of potash, the quantity of carbonic acid driven off is such that the oxygen contained in the carbonic acid expelled is equal to that of the silicic acid used. This formula, SiO_2 , agrees with arguments derived from the specific gravity of the vapours of chloride and fluoride of silicon. The last formula, SiO , originally suggested by Dr. THOMSON‡, has been supported by M. DUMAS§, and also by EBELMEN||, from arguments suggested by the constitution of the silicic ethers.

* Ann. de Chim. &c. 3 sér. xxiv. 286.

† On Titanium and its Compounds, GILBERT's 'Annalen,' lxxiii. 83.

‡ System of Chemistry, 5th ed. 1817.

§ Ann. de Chim. &c. 2 sér. xxxiii. 368.

|| Ann. de Chim. &c. 3 sér. xvi. 163.

With regard to the arguments in favour of the first-mentioned formula, derived from a consideration of the boiling-point of chlorides and bromides, I should mention that M. KOPP, since the publication of a notice by Mr. DUPPA communicated to the Royal Society by Dr. HOFMANN, has appended to a translation of this note some remarks of his own*, in which he states that the law he had suggested cannot now, in its primitive generality, be regarded as true.

From what has preceded it may be observed, that the only instance in which the formula of silicic acid has been sought for by a direct method, as for example, in which its equivalent has been determined by the quantity of some other acid displaced, is in the experiments of ROSE. These experiments, however, which are introduced incidentally in a memoir on titanitic acid, have not generally attracted the attention of authors of chemical systems, but as it appeared to me that the method deserved preference over the others which have been used, or any that I could devise, I resolved to repeat the experiments, entertaining the notion that if the results were confirmed, this ought to establish the formula which they had suggested to ROSE.

I imagined that with the means I meant to apply, what I had in view would prove an easy matter; in this I was deceived; but though I am still unable to give a definite answer to the question which I had proposed to myself, I have obtained some results which I venture to think have interest, and which, under the uncertainty I am in of the time it may take before I can complete these researches, I desire to offer to the Society in their present state.

*Experiments on the quantity of Carbonic Acid expelled from excess of
Alkaline Carbonates by fusion with Silica.*

The silicic acid used was obtained by the ignition of perfectly transparent and colourless rock-crystal, and subsequent reduction of this to powder. The carbonate of potash was produced by the ignition and subsequent fusion of crystallized bicarbonate of potash. The carbonate of soda was mostly obtained by a similar treatment of the purest bicarbonate I could procure, though a few experiments were made with some carbonate obtained by the purification of the crystallized carbonate, by GAY-LUSSAC'S method.

In my earlier experiments I adopted methods varying a little from one another, of adding the silicic acid to the alkaline carbonate, whilst in a state of fusion, in a platinum crucible; after some experience I found that it was in all respects a better plan to add the alkali to the silica. The latter was placed in a counterpoised platinum crucible, and weighed; the fused alkaline carbonate in fragments was then weighed in a counterpoised closed glass tube, then gradually added to the silica heated in the crucible, and the tube again weighed, by which the quantity of alkaline carbonate was determined. The heating was performed by a gas-flame, through which a stream of air was forced by means of a table bellows. The crucible was heated for some time after all effervescence had ceased, and the materials used appeared in a quiet state of fusion. The crucible

* Ann. de Chim. &c. 3 sér. xlvii. 66.

was weighed when cold, and again heated for five minutes until the last two weighings agreed within a few hundredths of a grain. The loss was then estimated as carbonic acid. The equivalent of the silicic acid is then readily obtained by the following proportions, 22 being the equivalent of carbonic acid on the hydrogen scale:—

$$x = \frac{22 \times \text{weight of silica used}}{\text{weight of carbonic acid expelled}}.$$

Experiments with Carbonate of Potash.

No.	Quantities used.		Loss=Carbonic Acid.	Equivalents of Silica deduced.
	Carbonate of Potash. grs.	Silica. grs.		
I.	52	10·67	7·5	31·3
II.	61·3	13·45	9·62	30·06
III.	30·7	10·07	7·04	31·4
IV.	47·4	10·10	7·26	30·06
Mean				30·07

This result agrees very nearly with that of ROSE, and also with the formula SiO_2 , which, if calculated from the percentage composition of silicic acid as stated by BERZELIUS, would give 30·75. If from that assigned to it by PELOUZE, it would be 30·22.

Experiments with Carbonate of Soda.

No.			Loss=Carbonic Acid.	Equivalent of Silica deduced.
	Carbonate of Soda. grs.	Silica. grs.		
I.	58·16	13·08	13·7	21
II.	59·12	12·17	12·15	22
III.	60·68	13·86	13·94	21·8
IV.	53·04	16·45	15·2	23·7
V.	34·84	9·06	11·3	17·6
VI.	55·78	15·85	15·89	21·2
VII.	59·12	16·1	16·34	21·7
Mean				21·3

Here then I obtained a very different result from that with carbonate of potash, agreeing more nearly with half the number represented by the formula

$$\text{SiO}_3, \text{ or } \frac{45\cdot2}{2}.$$

As M. JACQUELAIN had stated that under certain circumstances carbonate of soda lost part of its carbonic acid by fusion*, I made the following experiments to ascertain whether, in my method of experimenting, the loss I had observed could be attributed to the action of heat alone. A portion of the carbonate of soda used in the last-mentioned experiments was fused for three or four minutes, it weighed=78·5 grs.

* Ann. de Chim. &c. 3 sér. xxxii. 195.

I. Fused a second time by gas-flame, urged by bellows for fifteen minutes, crucible open	} = 78.29	grs. diff. 0.21
II. Fused a third time by gas-flame, urged by bellows for fifteen minutes, crucible open	} = 78.26	0.03

On the following day,—

III. Fused a fourth time by gas-flame, urged by bellows for fifteen minutes, crucible open	} = 78.20	0.06
IV. Fused a fifth time by gas-flame, urged by bellows for fifteen minutes, crucible open	} = 78.14	0.06

The carbonate of soda had acquired a slight brown tint; on examination I found that this was owing to its containing a very minute portion of oxide of platinum derived from the crucible. From these experiments, it will be evident that the results I had obtained by the fusion of carbonate of soda with silica could not be accounted for by the action of heat alone.

The carbonates of potash and soda having afforded me such different results, I now had recourse to carbonate of lithia.

Experiments with Silica and Carbonate of Lithia.

The carbonate of lithia, as purchased, was purified by dissolving it in 100 parts of boiling distilled water, filtering the liquid from small portions of lime and other matters which remained undissolved, and evaporating the filtrate in a porcelain basin until a small portion of liquid only remained; the carbonate of lithia was obtained as a crystalline crust deposited on the basin. The mother-liquor contained potash.

The carbonate of lithia thus obtained was fused in a covered crucible. It lost very little weight. I found that although carbonate of lithia by itself fused at a temperature below a red heat, visible by daylight, yet that when any considerable proportion of silica was added, the fusing-point rose so much that I was obliged to conduct the experiments in a platinum crucible.

Experiments with Carbonate of Lithia.

No.	Carbonate of Lithia. grs.	Silica. grs.	Loss = Carbonic Acid.	Equivalent of Silica deduced.
I.	34.46	10.33	14.9	15.2
II.	26.87	8.24	12.09	14.99
III.	42.74	15.84	23.24	14.99
IV.	31.28	9.14	13.61	14.77
Mean				14.99

Experiments III. and IV. were made with a different specimen of carbonate of lithia from Nos. I. and II.

Hence it appears that the equivalent for silica, deduced from experiments with car-

bonate of lithia, differs from that obtained with the carbonates of the other two fused alkalies, and agrees with the formula SiO .

These unexpected results suggested to me two lines of research, by following which I hoped that some light might be thrown on the apparent anomaly involved in them. The first was to determine whether any other acid than the silicic yielded results similar to those already obtained with carbonates of potash and soda; and the second was to ascertain whether the equivalent of silicic acid could be obtained by means of any other volatile acid than the carbonic.

I desired to ascertain, in the first place, whether at the temperature used, any quantity of carbonic acid, different from its received equivalent, could be expelled by a well-known acid of the class of hydrogen acids, as *e. g.* the sulphuric acid. But as it was obviously impossible to experiment with this substance in its usual form, and considering that carbonate of magnesia could not exist at the temperature of the experiments, I made use of anhydrous sulphate of magnesia for my purpose.

With this substance I made the following experiments:—

With Carbonate of Potash and Sulphate of Magnesia.

No.	Carbonate of Potash. grs.	Sulphate of Magnesia. grs.	Loss = Carbonic Acid.	Equivalent of Sulphuric Acid deduced.
I.	58·14	27·81	10·51	39·4
II.	63·99	32·11	11·44	41·0
			Mean	40·2

With Carbonate of Soda.

	Carbonate of Soda.			
I.	43	30·27	11·3	39·4
II.	60·9	34·46	12·22	41
III.	67·98	35·28	12·63	40·1
			Mean	40·1

The number 40 is the received equivalent of sulphuric acid. These experiments are sufficient to show that with sulphuric acid, at the temperature used, no such effect as that with silicic acid is obtained.

I made several experiments of the same kind with tungstic acid, with boracic acid (using, however, biborate of soda for the purpose), alumina, and red oxide of iron. Boracic acid only, of the bodies named, afforded results analogous to those given by silicic acid, but I did not succeed in obtaining numbers which accorded well together. The other substances mentioned gave like results, whether carbonate of potash or soda was employed. As alumina appears in some instances to take the place of silica, I will insert here the results I obtained with that body.

The alumina was obtained by GREGORY'S process.

Experiments with Carbonate of Potash.

Carbonate of Potash. No. grs.	Alumina. grs.	Loss=Carbonic Acid.	Equivalent of Alumina deduced.
I. 46·98	21·2	9·15	50·9
II. 48·28	21·16	9·05	51·4
		Mean	51·1

With Carbonate of Soda.

Carbonate of Soda.			
I. 46·12	20·03	8·83	51
II. 52·21	27·18	11·93	50
		Mean	50·5

The equivalent usually assigned to alumina is 51·4.

Turning now to experiments made with the view of obtaining the equivalent of silicic acid in the weight of some other acid than the carbonic, I made some attempts with chloride of sodium and sulphate of soda, but with these did not succeed; I then had recourse to the hydrates, and will give the results I obtained. But I must premise that the difficulties of obtaining accordant quantities are much greater with these bodies than with the carbonates, difficulties which arise from the volatility of the alkalies on the one hand, and the tendency to absorb carbonic acid during the experiments on the other.

Of the various methods which I tried, I think that the best and simplest was to fuse the alkaline hydrate and weigh it in a deep narrow silver crucible provided with a cover, and of large capacity compared with the bulk of materials employed, then to add the silica and weigh the two bodies together; to heat this crucible while much inclined very gradually, and finally to repeat the weighings and heatings until the weight appeared constant. The last two experiments with hydrate of soda were made in this manner.

Experiments with Silica and Hydrate of Potash. Water=9.

Hydrate of Potash. No. grs.	Silica. grs.	Loss=Water.	Equivalent of Silica deduced.
I. 73·27	18·39	5·39	30
II. 105·39	19·22	4·7	36·7
III. 96	16·08	4·95	29·2
IV. 87·44	6·55	1·8	32·7
V. 70·38	7·37	2·39	27·7
VI. 74·7	7·65	2·59	26·1
		Mean	30·8

With Silica and Hydrate of Soda.

No.	Hydrate of Soda. grs.	Silica. grs.	Loss = Water.	Equivalent of Silica deduced.
I.	100·04	18·61	9·18	18·2
II.	81·29	10·07	5·48	16·4
III.	128·24	15·86	8·37	17·0
Mean				17·2

In these experiments with the hydrates, it will be observed that the equivalent obtained with hydrate of potash is the same as that obtained with the carbonate, but that obtained with hydrate of soda approaches more nearly to that afforded by carbonate of lithia.

Reverting now to the experiments with the carbonates, I found that I had, in order to secure the requisite fusibility in the case of the carbonate of lithia, used a greater proportion of that salt to the silicic acid than with the other two carbonates, so that considering the ratio of the oxygen in the base to that in the silicic acid in the case of the lithia experiments, it was nearly as 2 : 1, whilst in the other two carbonates the oxygen was equal in the base and in the silicic acid. To ascertain if this would in any way explain the results I had obtained, I made two experiments with carbonate of potash, in which the oxygen, considered as belonging to the oxide of potassium, was double that contained in the silica, and obtained for the equivalent the number 29 very nearly. Operating in a similar manner with carbonate of soda, the mean of two experiments gave 19·5.

Both the numbers thus obtained are slightly smaller than those given in the former experiments, but I do not think they should materially affect any inference to be drawn from them; and I may remark here, that, though I am of opinion that generally the quantity of carbonic acid expelled by an anhydrous acid from the alkaline carbonates in fusion may be very valuable for determining between two different formulas for such acid, I do not think that the method is capable of determining with precision the equivalent weight of such an acid, as I have satisfied myself in the course of these experiments, that when the heat is long-continued, minute, but appreciable quantities of the alkali are volatilized.

On Crystallized Hydrate of Silicate of Soda.

A silicate of soda was formed by taking one equivalent of carbonate of soda, or 54 parts, and one equivalent of silica as given by the results of the experiments before detailed, or 23 parts, and fusing them together, the quantity of carbonic acid present would be 22; the quantity actually expelled was 20, so that 2 parts = 5 of carbonate of soda had remained in the fused mass. This substance appeared crystallized throughout, and to be made up of spheroidal masses of prismatic crystals radiating from a centre. This kind of crystallization invariably followed on fusing together the two substances in

the proportions I have mentioned. The fused substance readily dissolved in water, affording a perfectly colourless transparent solution. The solution was evaporated at atmospheric temperatures *in vacuo* with sulphuric acid; after some days it began to crystallize, and eventually formed a mass of crystals with very little liquid remaining.

Analysis.

I. 17·62 grs. of the salt, dried by pressure in filtering paper, was treated with hydrochloric acid, effervescence was produced. It yielded 3·72 grs. of ignited silica. The filtrate evaporated and residue ignited, gave 8·33 grs. chloride of sodium = 4·41 soda.

II. 16·24 grs., dried as before, heated on a sand-bath, melted into a clear liquid, which soon became viscid and opaque; ignited, it weighed 7·78 grs.; loss = 8·46.

III. 22·17 grs. of the salt, dried as before, heated red in a platinum crucible = 10·66; loss = 11·51.

To expel the carbonic acid, a little silica was added to the remaining substance, the whole = 13·78.

This was heated by the gas-flame, urged by bellows for ten minutes, and	}	= 13·28
then weighed		
		Loss = carbonic acid = 0·50

These experiments would give as the constituents of 100 parts of the salt (a),—

	I.	II.	III.
Silicic acid	21·11	—	—
Soda	25·02	—	—
Carbonic acid and } 53·87 {		—	2·25
water by loss . }		52·1	51·90

and as 2·25 carbonic acid would combine with 3·15 soda, 100 parts would contain—

Silicic acid	21·11
Soda	21·87
Carbonate of soda	5·40
Water	51·90
	100·28

If the carbonate of soda be the ordinary ten-hydrated salt, and this be considered as mixture and subtracted, we obtain—

	By Theory, in 100 pts.	By Experiment, in 100 pts.
SiO ₂	24·19	24·61
Soda	25·01	25·49
7HO	50·80	49·90
	124·2	

Two crystallized hydrates of silicate of soda have been described by FRITZSCHE*, one of which crystallizes in rectangular prisms, and contains 56·6 per cent. of water, the other 47 per cent. HERMANN† has also described a salt of this kind crystallizing in rhombohedrons and containing 54·4 per cent. of water. In all these salts the proportion of acid to base is the same as in the one I have described above, and the number of equivalents of water contained in them respectively is 9, 6 and 8. Lately M. FREMY‡, in a communication on the Silicates, has described a silicate which he states he obtained in large crystals, to which he assigns the formula $(\text{SiO}^2)^3 4\text{NaO}, 26\text{HO}$, which would give 48·6 per cent. of water. I regret that I have not been able to determine the crystalline form of the salts I have obtained; but the point to which I wish to direct attention is, that in the process of obtaining a crystallized hydrate from the fused anhydrous salt a portion of soda is extruded. I found that this extrusion also took place when the salt was formed by dissolving hydrated silica in such a quantity of a solution of caustic soda, as that the soda should be in the same proportion to the silica as in the fused salt before described, viz. as 31 : 23.

A specimen of a crystallized salt, formed in this manner, of which the solution had been exposed to the atmosphere during crystallization, yielded, on analysis,—

Silica	22·38
Soda	24·44
Carbonate of soda . .	2·41
Water	50·55

I also obtained a crystallized salt by dissolving silica in a solution of caustic soda in such proportion that the oxygen in the silica should be double that in the soda. The crystallized salt was redissolved and recrystallized, the crystallization in both instances taking place out of contact with the atmosphere.

Analysis gave the following composition of this specimen (c):—

Silica	24·45	2SiO	} give	30·2	in 100.	24·193
Soda	25·276	NaO		31		25·00
Water	50·374	7HO		63		50·80

As it appeared to me desirable to ascertain if any portion of the water in these salts should be considered as basic, I made some experiments on specimens (a) and (c) with this view. I found however no decided difference in the comportment of the two specimens; and further, that all the water, with the exception of less than 1 per cent., was expelled at a temperature of 300° FAHR.

With regard to the silicate of lithia (LiO, SiO), I have not yet been able to examine it particularly; but when treated with water it appears, like the soda compound, to split into different combinations, as a substance which remained when more than one-half of

* POGGENDORFF'S Annalen, xliii. 135.

† ERDMANN'S Journal für prakt. Chemie, xiv. 275.

‡ Comptes Rendus, December 1856.

the salt had been washed away, gave a result on analysis showing that its silicic acid contained at least double the quantity of oxygen contained in the lithia.

As to the formula SiO , deduced from the lithia compound, I would add, that some observations have lately been published by TROOST*, which go to show that lithia in its comportment has more analogy with the magnesian class of bases than with the potassium class. Now, of the known crystallized silicates of bases belonging to the former class, whether found in nature or obtained in the processes of the arts, a large proportion have a composition in which the oxygen of the base is equal to that of the acid.

In concluding this paper, I desire to guard myself against drawing any decided inference from the experiments I have related, particularly as I hope to be able to follow up this communication by further researches, which may afford more definite grounds for theory. I venture only to remark at present, that as I cannot but think that the quantity of carbonic acid displaced must afford a true measure of the equivalent of silicic acid; so, looking to the results of my experiments, I see at present no alternative but to admit of at least two equivalents (that is to say, of two acids), the value of which is determined by circumstances, such as the presence of water, and the nature of the base to which the silicic acid is presented.

The existence of different silicic acids has been already suggested by chemists, particularly by EBELMEN† and by LAURENT‡. FREMY also considers that his late experiments, before quoted, support the same view.

* Comptes Rendus, November 10, 1856. Chemical Gazette, December 1856.

† Ann. de Chim. &c. 3 sér. xvi. 162.

‡ Chemical Method, Engl. Trans., p. 127-8.